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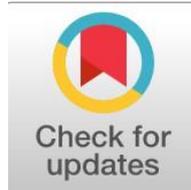
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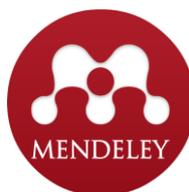
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Synthesis and Characterization of PMMA-PS Blend with Various Bi₂O₃ Nanoparticle Additives: Structural, Optical, Electrical, and Biological Properties

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Abstract

General Background: Polymer-based nanocomposites have attracted significant attention due to their multifunctional properties and broad applicability in advanced materials science. **Specific Background:** Blending polymethyl methacrylate (PMMA) and polystyrene (PS) with bismuth oxide (Bi₂O₃) nanoparticles provides a promising route to develop materials with combined structural, optical, electrical, and biological functionalities. **Knowledge Gap:** However, systematic understanding of how varying Bi₂O₃ nanoparticle concentrations affect the multifunctional properties of PMMA-PS nanocomposites remains limited. **Aims:** This study aims to synthesize PMMA-PS/Bi₂O₃ nanocomposite films with different nanoparticle loadings (0, 1, 3, and 5 wt%) and evaluate their structural, optical, electrical, and antibacterial characteristics. **Results:** The findings reveal uniform dispersion of Bi₂O₃ nanoparticles, reduced optical bandgap from 2.9 to 2.6 eV, increased refractive index, and improved DC electrical conductivity due to enhanced charge carrier mobility. Additionally, nanocomposites containing 5 wt% Bi₂O₃ exhibit strong antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*. **Novelty:** This work demonstrates a comprehensive correlation between nanoparticle concentration and multifunctional performance in PMMA-PS/Bi₂O₃ nanocomposites. **Implications:** The developed materials show potential for applications in optoelectronic devices, humidity sensing, biomedical technologies, and environmental systems.

Highlights:

- Uniform Nanoparticle Dispersion Confirmed by Structural and Morphological Characterization
- Optical Bandgap Reduction Accompanied by Refractive Index Increase
- Highest Nanoparticle Loading Exhibits Strong Antibacterial Performance

Keywords: PMMA-PS/Bi₂O₃ Nanocomposites, Optical Bandgap, Electrical Conductivity, Antibacterial Activity, Polymer Blends.

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Introduction

Recently, the hybrid polymeric thin films have developed significantly due to their great potential in the field of biomedical applications, and especially as a protective coating, biosensing and drug delivery systems [1]. Some of the most famous and widely used polymers in the field of biomedical engineering are (PMMA) and polystyrene (PS). This high status and value were acquired for several reasons, including optical transparency, biocompatibility and mechanical stability [2]. Impregnated polymer films are composite materials in which nanoparticle fillings are distributed in a fixed and stable manner within the polymer matrix. This is due to their special and exceptional physical, chemical, and electronic properties [3].

Poly methyl methacrylate (PMMA) It is a synthetic polymer. This polymer is a transparent thermoplastic coating, also known as acrylic, currently used in the field of cosmetic medicine, where it is widely used in nail polish. It also has well-known trade names and brands such as Crylux, Walcast, Heselite, and Plexiglas, Acrylite, Lucite, Per Clax, and Perspex, among several others [4]. **PS (Polystyrene)** It is a polymer manufactured in a laboratory from certain materials. It can be in foamed or a solid status. It has many properties, including being transparent, hard, brittle, relatively inexpensive, having a low melting point, and having weak air and water vapor retention [4,5]. Annual production for polystyrene exceeds millions of tons. Annual production exceeds millions of tons and is characterized by its transparency to visible light, with the possibility of coloring it with known colors [6]. It is used in protective packaging (such as packing peanuts and optical disc jewel cases), as well as in the manufacture of disposable cookware such as cups, spoons, and pots, and also in the glass industry [7,8]. **Bismuth (III) oxide** It is one of the most famous and important bismuth compounds in bismuth chemistry and occurs naturally as the mineral bismuth (monoclinic) and sphalerite (tetragonal, much rarer) [9]. It is used very effectively as a substitute for red lead in the production of fireworks and also in the production of dragon eggs, which are also a type of firework. All these uses belong to dibismuth trioxide [9,10]. This type is historically called acrylic glass because it is a non-crystalline glass material and is practically classified as a type of glass [11].

There is potential to enhance the physical and chemical properties of the material, making it highly suitable for biomedical applications, through blending PMMA and PS. Bismuth oxide is a wide-bandgap semiconductor known for its high ionic conductivity, thermal stability, and flexibility [12].

The study aims at the fabrication of PMMA-PS by doping it with different (varying) concentrations of Bi₂O₃ nanoparticles through solution casting and spin coating techniques. The objective is to evaluate the structure properties, morphological, optical, electrical, and potential biological properties of the resulting nanocomposite films, aiming to determine their suitability for biomedical applications. By understanding the influence of Bi₂O₃ doping on the hybrid polymer matrix, this work aims to the advance of functional biomaterials with enhanced performance and targeted functionalities [13].

Experimental Materials

PMMA was obtained granules as a base polymer were purchased from "Xiamen Keyuan" Plastic Co, China. Also, PS granules as a base polymer were obtained from trah Ab polymer in Iran and Bi₂O₃ nanoparticles purity 99% and size (30-50) nm as nano fillers were commercially purchased from Merck Materials, Germany. The main characteristics of the PMMA, PS and nanoparticles from the manufacturer's data are listed in Tables 1, 2 and 3, respectively [14,15].

Table 1. Properties of PMMA [13].

| Properties | Unit | ASTM standard | Value |
|------------------------------|--------------------|---------------|--------|
| Density | g/cm ³ | D-792 | 1.19 |
| Melt flow rate | g/min | D-1238 | 1.48 |
| Tensile strength | kg/cm ² | D-638 | 10,200 |
| Flexural strength | kg/cm ² | D-790 | 15,600 |
| Elongation at break | - | D-638 | 5% |
| Izod notched impact strength | kJ/m ² | D-256 | > 25 |
| Heat deflection temperature | °C | D-648 | > 100 |

Table 2. Properties of PS [14,15].

| | |
|---------------------------|----------------------------|
| Density | 1050 kg/m ³ |
| Electrical Conductivity | 10 ⁻¹⁶ S/m |
| Thermal Conductivity | 0.08 W/(m-K) |
| Tensile Strength | 46-60 MPa |
| Glass Temperature | 95°C |
| Melting Point | 240°C |
| Heat Transfer Coefficient | 0.17 W/(m ² -K) |
| Specific Heat | 1.3 kJ/(kg-K) |

Table 3. Physical properties of nanoparticles [15].

| Nanoparticles | Purity (%) | Size (nm) | Density (g/cm ³) | Shape and color |
|--------------------------------|------------|-----------|------------------------------|-----------------|
| Bi ₂ O ₃ | 99% | 30-50 | 8.93 | Yellow, white |

Preparation PMMA-PS/ Bi₂O₃ Films

In this work, granular polymethyl methacrylate (PMMA) polymer was used and dissolved in chloroform for three hours on a magnetic stirrer. Polystyrene (PS) polymer was then added for four hours, also on a magnetic stirrer, to achieve good homogeneity. Bicarbonate oxide (Bi₂O₃) nanoparticles were gradually added to prevent agglomeration at different weight percentages (1,3 and 5) wt.%, and ultrasonically at 80°C. These nanoparticles acted as UV absorbers to improve the polymer's properties. The effect of the bicarbonate oxide nanoparticles on the optical properties of the prepared coatings was also investigated [11].

PMMA-PS/ Bi₂O₃ film characterization

1. Sturcture properties

Images were verified using a scanning electron microscope (MIRA TESCAN, Czech Republic) at 15 kV to determine the thin-film surface morphology. A thin gold coating was applied, and images were scanned at 100,000x magnification. using X-ray diffraction (XRD) The film's properties were determined and characterized (Philips X'Pert High Score device , PANalytical and Netherlands) with Cu K α radiation ($\lambda = 0.1542$ nm), scanned over a 2 θ range of 10–80°and operated at 40 kV.[15]

2. Optical properties

It was studied verified using a UV-Vis spectrometer (Shimadzu UV-1800A) to record the transducer in the 200–1100 nm range. The optical properties of PMMA-PS films doped with different concentrations of Bi₂O₃ nanoparticles were investigated using UV-Vis spectroscopy[16,17].

2-1- Absorbance and absorption coefficient

There is a direct relationship between between the absorption value and the concentration; increasing one leads to an increase in the other, and vice versa. The absorption coefficient (α in cm⁻¹) was calculated using the equation below (Equation 1)[18]. The relationship between the absorption coefficient and concentration was also directly proportional (increasing the absorption coefficient leads to an increase in concentration, and vice versa)[18].

$$\alpha = 2.303 \frac{A}{t} \dots \dots \dots (1)$$

Here A represents the absorbance measured at a given wavelength, and t is the thickness of the film in centimeters (~33 μ m for the PMMA-PS blend for the PMMA-PS/Bi₂O₃ nanocomposites).

2-2- Extinction Coefficient and Refractive Index

The extinction coefficient (k)and the refractive index (n) were calculated using equations)2and 3) and, respectively [19,20].

$$k = \frac{\alpha \lambda}{4\pi} \dots \dots \dots (2)$$

$$n = \sqrt{\frac{4R - k^2}{(R - 1)^2} - \frac{(R + 1)}{(R - 1)}} \dots \dots (3)$$

2-3- Band Gap Energy Eg

Using the Tauke model, the optical bandgap energy Eg of the prepared grafted films was studied [21].

$$\alpha h\nu = B(h\nu - E_g)^{\frac{1}{2}} \dots \dots \dots (4)$$

where B is constant related to the type of the film.

3. The electrical characteristics)DC) of PMMA-PS- nanocomposites.

Electrical properties were determined using a digital multimeter, a Keithley 2450 DC (DMM), with the source unit of measurement (SMU). The pulse used for reading was set to 200 microseconds, and the time between the reading pulse and the writing pulse was 700 microseconds[22]. The DC conductivity of PMMA-PS polymer was calculated using Equation (5) [23].

$$\sigma_{DC} = \frac{1}{\rho_V} = \frac{t}{R_V A_s} \dots \dots \dots (5)$$

where represents the volume resistivity, denotes the volumetric electrical resistance, t is the sample thickness, and is the surface area of the sample. The main criterion that electrons use to cross energy barriers to contribute to conduction is the

thermal activation energy of PMMA-PS-/Bi₂O₃ nanocomposites, which was calculated using equation (6)[23].

$$\sigma_{DC} = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \dots \dots (6)$$

where σ_{DC} is the electrical conductivity extrapolated to absolute zero temperature, k_B denotes the Boltzmann constant, and E_a represents the activation energy .

4. Antibacterial Activity

Bacterial susceptibility testing: 5 mg of quinazolinone derivatives and polymers, as well as PMMA/PS/Bi2O3, were dissolved in 1 ml of dimethyl sulfoxide (DMSO). Different concentrations were added in a specified amount (nutrient agar, 28 g/L, pH 7.4). The media were sterilized by autoclaving and then poured into 3-4 mm deep Petri dishes. Organisms were then cultured in the dishes. The wells were then filled with 100 µL of the test compounds, and the dishes were incubated at 37°C for 24 h. DMSO was used as a buffer with a zero inhibition zone. PMMA-PS/Bi2O3 nanoparticles, which act as an antifungal, were sensitized at different concentrations with the polymer against the reference strain *Candida albicans* (ATCC 10231). *Candida albicans* were cultured in SDA plates for 2–5 days before eradication. They were incubated at 37°C for 2 days. The colonies were then purified and isolated in 20 ml of broth medium. Furthermore, they were incubated overnight with shaking at 30°C to produce approximately 1×10⁸ CFU/ml at 0.5 McFarland spoonful’s of yeast.

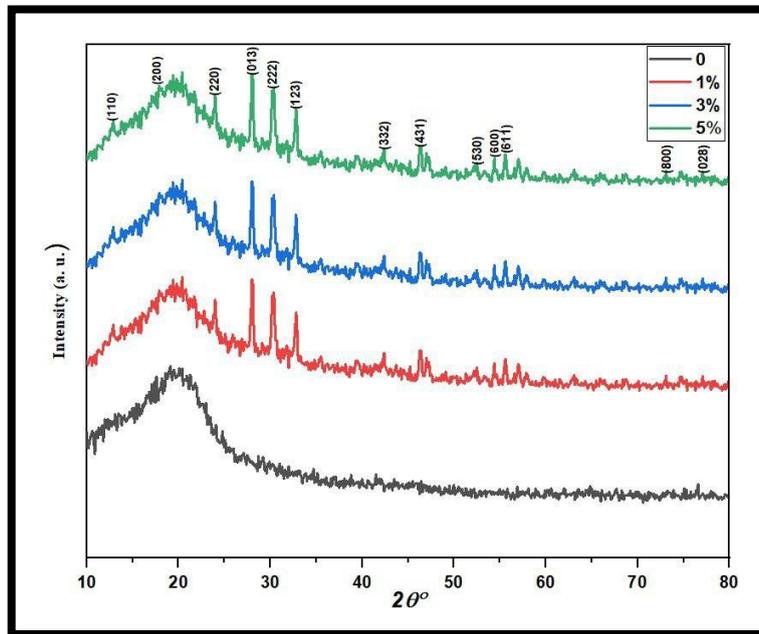
Results and Discussion

1- X-ray diffraction analyses

X-ray diffraction patterns were recorded from mixing composite nanomaterials containing (1, 3, and 5 wt) with PMMA-PS polymer to determine the crystalline nature of the compounds present in the composite nanomaterials.% Bi2O3 nanoparticles, as shown in Figure 1. The quasi-crystalline nature of the PMMA-PS polymer causes it to exhibit a wide diffraction range, and this range confirms the polymer's (quasi-crystalline) nature.

Additional diffraction peaks are observed in micro-X-ray diffraction of various compounds when Bi2O3 nanoparticles are added.. The X-ray diffraction pattern of γ -Bi2O3 shows peaks at 2 θ values of 12.9°, 17.6°, 24°, 28 °, 30.2°, 32.8°, 42.3°, 46.9°, 52.21°, 54.4°, 55.6°, 73.1°, and 77.1°, which correspond to the crystalline planes (110), (200), (220), (013), (222), (123), (332), (431), (530), (600), (611), (125), (611), (800), and (028). are characteristic crystalline levels of the cubic Bi2O3 phase (Figure 1b), as identified in JCPDS card No. 74-1373 [24,25].

Figure 1. XRD patterns of the PMMA-PS / Bi2O3 nanocomposites (0, 1, 3 and 5) wt.%.



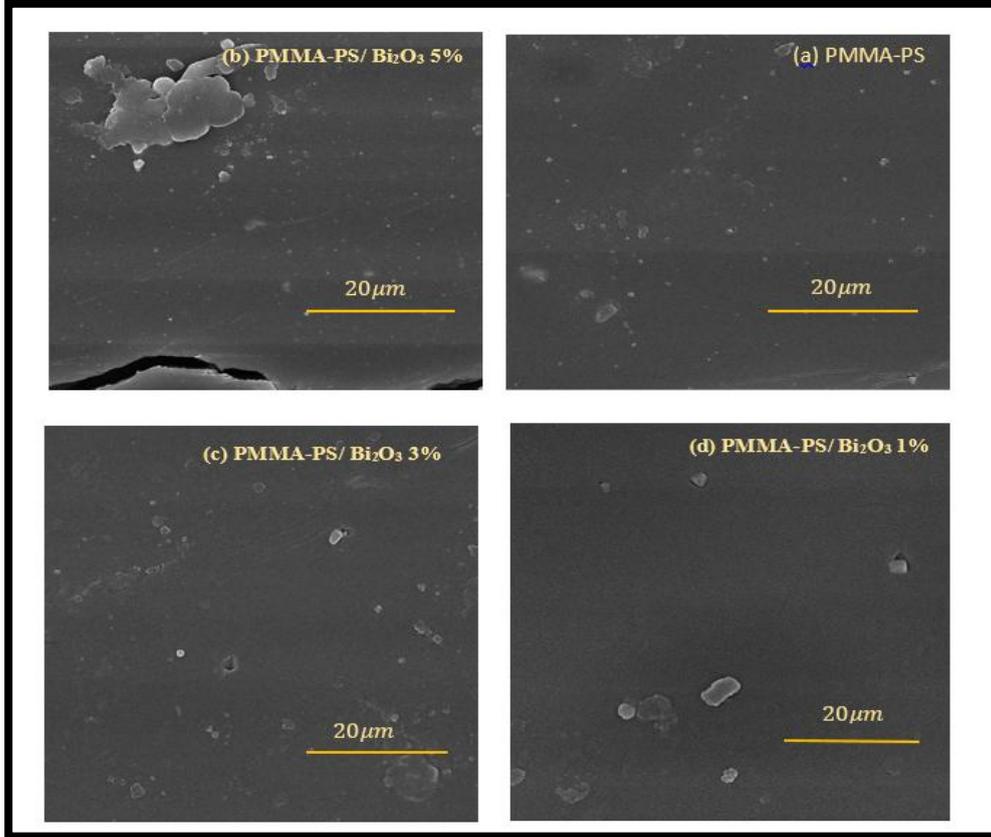
2- Scanning electron microscope

Controlling the orientation of the thin-homogeneous polymer layer towards the surface is abasic to using this material in the molding process. For example, the surface exhibits patterns (lines or spaces) that closely resemble fingerprints, allowing for a uniform distribution of bismuth oxide nanoparticles. For PMMA-PS, the directions of self-assembled pattern regions can be determined through the availability of several effective and proven surface treatments[26].

Due to the concentration of Bi2O3 nanoparticles, the self-assembly of PMMA-PS remains sensitive even under appropriate surface treatments. In the field of pattern forming using homopolymers to achieve alignment and recording of elements by guiding self-assembling zigzag fingerprint patterns, self-assembly technology was used."Surface morphology of PMMA-PS/

Bi₂O₃ NPs at 10 μ m magnification are presented in Figure 2. Figure 2-a shows that undoped PMMA-PS films exhibit an organized texture. Figure 2-b-d shows a small effect of the Bi₂O₃ NPs immersed in the thin film matrix on the surface of doped PMMA-PS nanocomposites films. Furthermore, we examine SEM micrographs to investigate the morphology and dispersion of Bi₂O₃NPs on the surface of PMMA-PS films. Good dispersion of Bi₂O₃ NPs on the surface of the PMMA-PS films is revealed. This provides substantial evidence of the validity of our synthesis process of obtaining Bi₂O₃ NPs"[27].

Figure 2. scanning electron microscope (SEM) cross sections of chemically developed images of films of (a) PMMA-PS (polymer blend), (b) PMMA-PS/ 5 wt.% Bi₂O₃ (c) PMMA-PS/ 3wt.% Bi₂O₃ , and (d) PMMA-PS/ 1wt.% Bi₂O₃.



3- UV-Vis analyses of PMMA-PS/Bi₂O₃ NPs nanocomposite

3-1- Absorbance and Absorption coefficients

Optical properties of PMMA-PS films doped with different concentrations of Bi₂O₃ nanoparticles were investigated using UV-Vis spectroscopy. Figure 3 shows the absorption of the composite PMMA-PS/Bi₂O₃ nanoparticle films [28]. The absorption spectra were observed at wavelengths of 200–350 nm at a 5% concentration and a wavelength of 250 nm, with the absorption peak reaching its highest value.

Figure 3. Absorbance of (PMMA-PS)/Bi₂O₃ nanocomposites with different Bi₂O₃ NPs concentrations

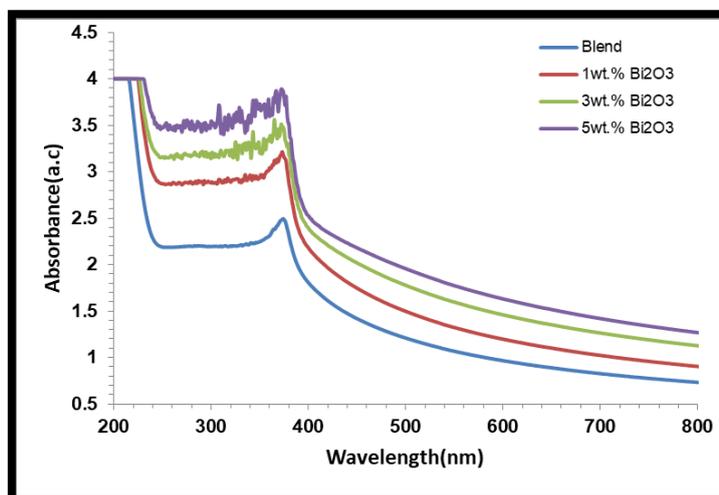
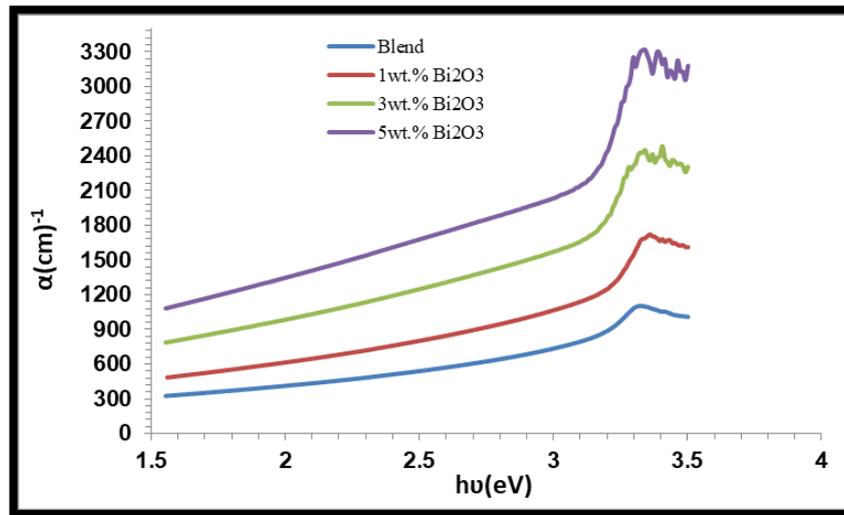


Figure 4. Absorption coefficients of (PMMA-PS)/Bi₂O₃ nanocomposite with different Bi₂O₃ NPs concentrations.



3-2- Extinction Coefficient and Refractive Index

New high performance novel materials with different applications in many industrial field can be produced using inorganic bismuth oxide (Bi₂O₃) nanoparticles within a polymer matrix. In this context, optical properties, such as light absorption, are frequently considered [29].

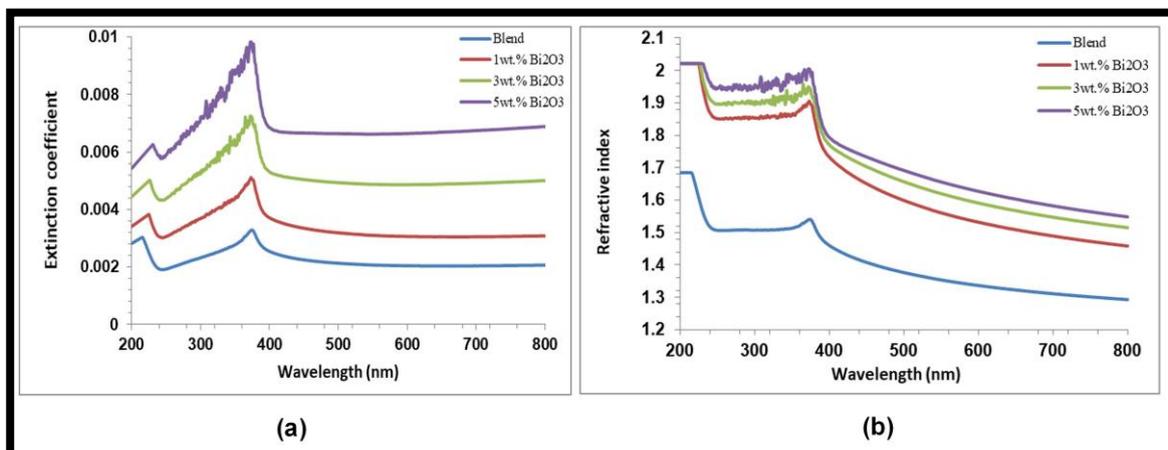
Figure 5a shows the calculated absorption coefficient(K) in the spectral range (200nm–800nm) as a function of the wavelength. In the spectral range (800 nm ≥ λ ≤ 200 nm), the absorption coefficient(k) is zero for all the thin-film samples studied; this means that the thin films allow the passage of electromagnetic waves without any attenuation or decay of photons with wavelengths (λ ≥ 200 nm).

In the high-frequency region, (200 ≤ λ ≤ 300) nm, the absorption coefficient increases and peaks at (230) nm. The reason for this is the very high absorption of high-energy electromagnetic waves, which are absorbed by waves whose energy is close to the optical bandgap energy of the composite nanothin film, to a large exten[30].

Refractive index (n) is generally connected to the local field and the electronic polarization of ions within optical materials. Optical applications of polymers are often confined because of their fairly narrow refractive index compared to inorganic solids. Polymer nanocomposites with extremely high refractive indices are produced by adding inorganic nanoparticles to a polymer matrix, opening up broad prospects for their applications in anti-reflective films, lenses, solar cells, optical filters, optical adhesives, and photoguides. Figure 5b shows that n for PMMA-PS ranges from 1.85 to 2 [31,32].

Introducing 1% Bi₂O₃ into the polymeric matrix causes a minor increase in n (1.85–2). As the Bi₂O₃ NPs concentration is increased to 3% and 5%, n continuously increases to (1.90–2) and (1.95–2). Consequently, (PMMA-PS)/Bi₂O₃ nano composite thin films could be potential candidates as excellent reflective material [33].

Figure 5. (a) Change in the refractive index and (b) the extinction coefficient as a function the wavelength (λ) of the different PMMA-PS)/ Bi₂O₃ nanocomposite films.



3-3 Band Gap Energy Eg

Using the Tauc model, the optical bandgap energy E_g of the prepared grafted films was studied. Figure 6 show the correlation between the energy of incident photons ($h\nu$) and $(\alpha h\nu)^{1/2}$. The optical band gap energy E_g of (PMMA/PS)/ Bi_2O_3 nanocomposite films with different Bi_2O_3 NPs concentrations are acquired by extrapolating the linear part of the Tauc plot to the interception of the incident photon energy [32]. Optical band gap energy of PMMA-PS is computed to be ($E_g = 2.9 \text{ eV}$) consistent with previously reported values [33]. As Bi_2O_3 the NPs concentrations is increased to 1%,3%and 5%, optical band gap decreases to (2.8,2.7, and 2.6) eV, respectively (see table 1). Thus, band gap engineering could be achieved effectively by inserting a specific concentration of Bi_2O_3 NPs in the polymeric films [32-35].

Figure 6. "The Tauc plot for energy band gap(E_g)" of containing various Bi_2O_3 NPs concentrations (PMMA-PS)/ Bi_2O_3 nanocomposites films.

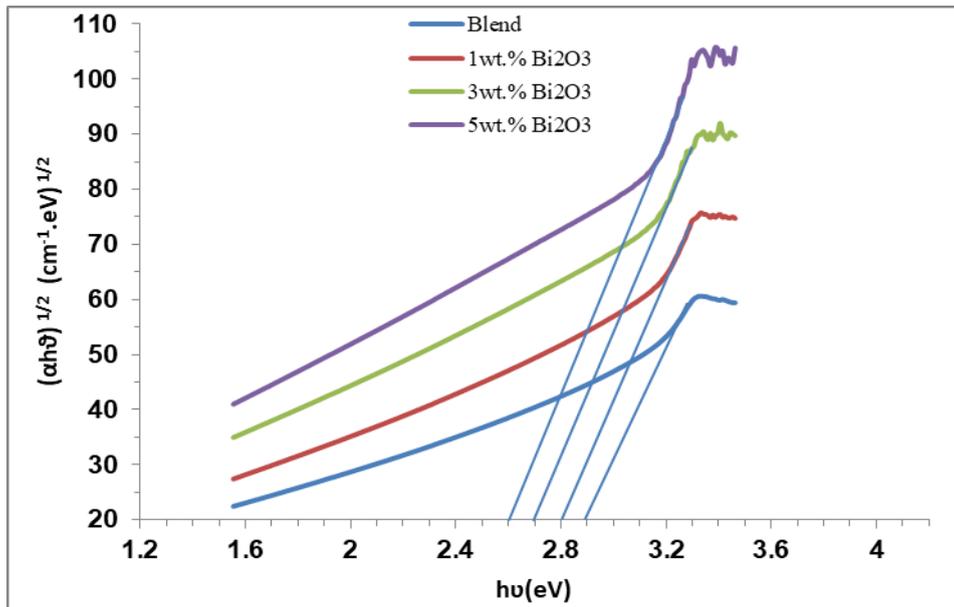


Table (1) . Optical band of (PMMA-PS/ Bi_2O_3) nanocomposite films containing different Bi_2O_3 NPs concentrations.

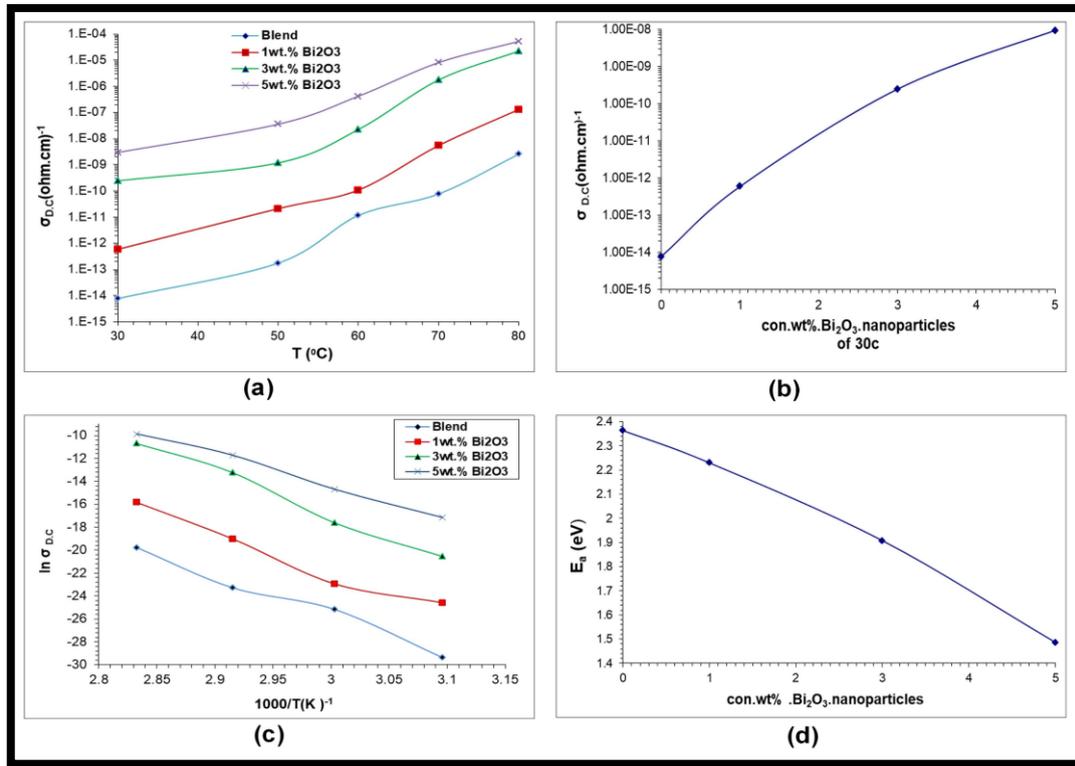
| Sample | Allowed $E_{g \text{ indir.}}^{\text{opt}} \text{ (eV)}$ Tauc relation |
|---------|---|
| Pure | 2.90 |
| 1 wt. % | 2.80 |
| 3 wt. % | 2.70 |
| 5 wt. % | 3.60 |

We investigated the DC electrical properties of PMMA-PS-based nanocomposites. These properties are crucial for determining the suitability of these materials for applications such as sensors and actuators. The DC conductivity of PMMA-PS polymer was calculated, and its variation with temperature and bismuth oxide (Bi_2O_3) content is shown in Figures 7a and 7b. We observed a significant improvement in the DC electrical conductivity of PMMA-PS polymer upon incorporation of bismuth oxide nanoparticles, particularly with increasing temperature. This marked improvement in conductivity is attributed to increased charge-carrier mobility and a higher nanoparticle content. As temperature and nanoparticle content increase, the number of charge carriers with higher kinetic energies increases.

These carriers undergo thermal jumping between local states, leading to improved conductivity [30-35]. Furthermore, incorporating of bismuth oxide (Bi_2O_3) increases the local energy levels within the mixture's band gap, thereby reducing the restricted energy gap and enhancing charge transport. The main criterion that electrons use to cross energy barriers to contribute to conduction is the thermal activation energy of PMMA-PS-/ Bi_2O_3 nanocomposites. The main criterion that electrons use to cross energy barriers to contribute to conduction is the thermal activation energy of PMMA-PS-/ Bi_2O_3 nanocomposites, which was calculated using equation (6) [23].

Figure 7c shows a graph of the relationship between $\ln(\sigma)$ and $1000/T$. The activation energy values for PMMA-PS-/ Bi_2O_3 nanocomposites were found to range between 2.55 and 1.37 eV, with the highest value observed for pure PMMA-PS. Increasing the bismuth oxide (Bi_2O_3) content leads to a decrease in activation energy. This is because local energy levels within the finite energy gap, as bismuth oxide concentration increases, contribute to the formation of a continuous conductive network within the polymer mixture, resulting in a lower activation energy [36].

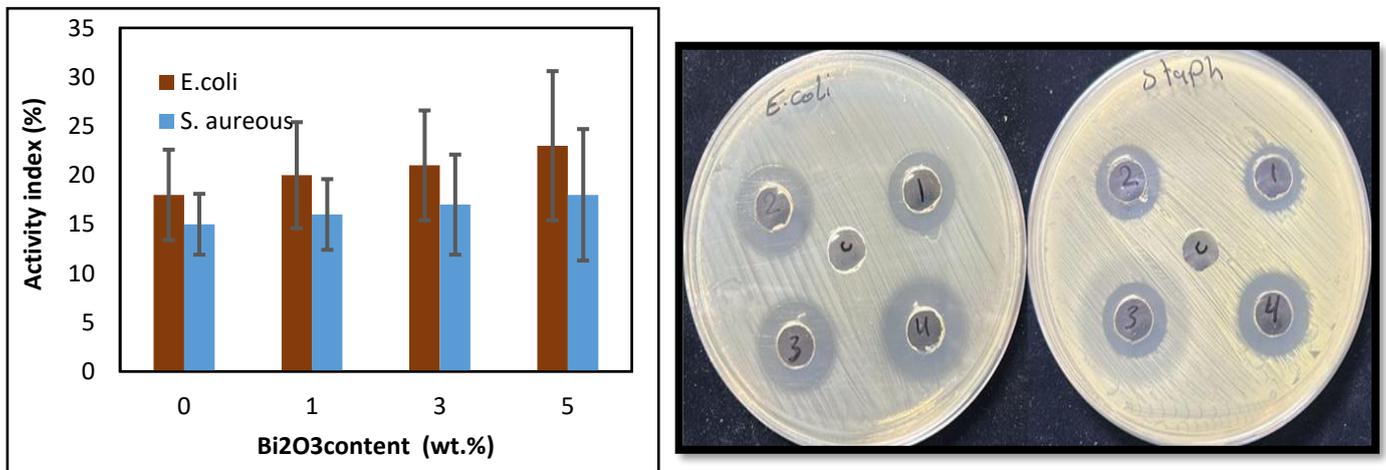
Figure 7. DC electrical properties of (PMMA-PS) and (PMMA-PS)/ Bi₂O₃ nanocomposite films: (a) electrical conductivity with temperature, (b) electrical conductivity with Bi₂O₃ contents, (c) plot of ln(σ_{DC}) and inverted absolute temperature, and (d) thermal activation energy.



4- Antibacterial Activity

The antibiotic was evaluated using the disk diffusion technique. The area of inhibition was measured using a ruler after 24 hours of incubation. As shown in Figure 8, Bi₂O₃ nanomaterials were used at different concentrations (1, 3, and 5%) with PMMA/PS blends. The sensitivity of materials depends on the concentration; the higher the concentration, the greater the inhibition. In this study, the antibacterial activity of PMMA-PS/Bi₂O₃ was demonstrated by disk diffusion assay to be greater against *Staphylococcus aureus* (Gram-positive) than against *Escherichia coli* (Gram-negative). Furthermore, ciprofloxacin at a concentration of 10 g/ml was used as a positive control. This study is positive and vital, as this material is biocompatible and can be used against microbes [38,39].

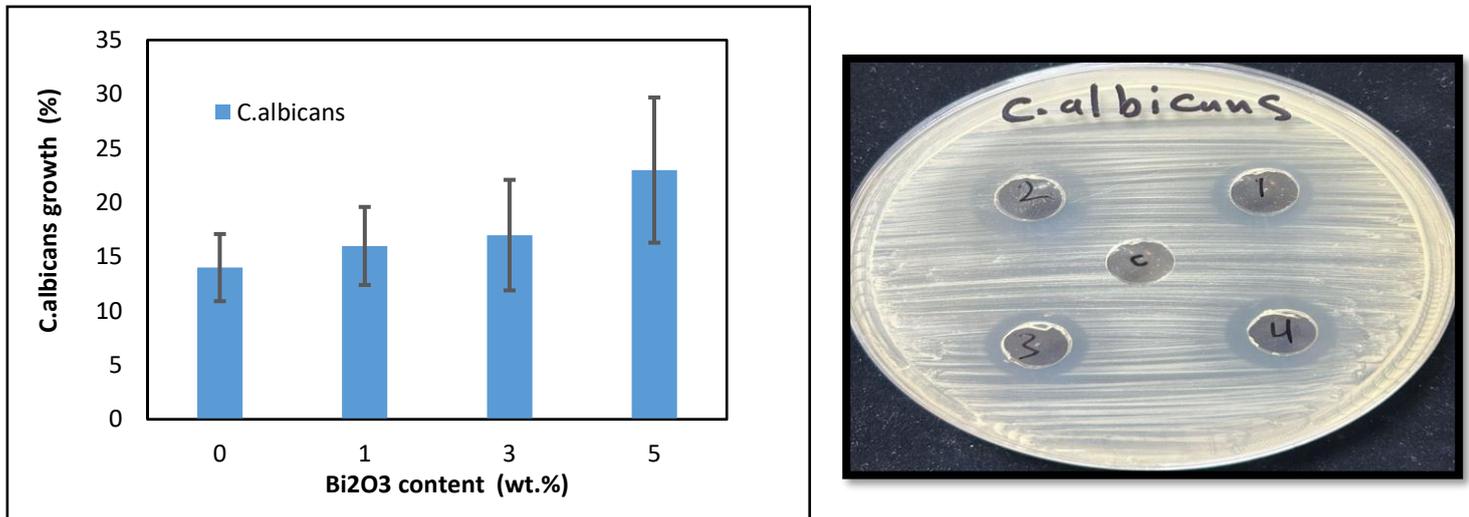
Figure 8. The disk diffusion technique was used to evaluate the antibiotic.



5- Fungicidal activity

The inhibition percentage was verified through a susceptibility test against *Candida albicans* (*Candida albicans*) as shown in Figure 9. The effective value for inhibiting *Candida albicans* was 0.05 Bi_2O_3 NPs. Different concentrations of 0, 1, 3, and 5% were used, with the PMMA-PS blend polymer representing 0%. We conclude from this test that the higher the nanomaterial content, the higher the inhibition percentage. This is a good indicator that the manufactured material has biological and antibacterial effectiveness [40-41].

Figure 9. Susceptibility test against *Candida albicans* (*Candida albicans*).



Conclusions

This study successfully fabricated and characterized PMMA-PS/ Bi_2O_3 nanocomposite films via casting, exhibiting significant improvements in structure properties, optical, electrical, and biological properties. The inclusion of Bi_2O_3 nanoparticles (0 –5 wt%) enhanced crystallinity. The optical bandgap decreased, together with a rise in the refractive index, indicating its suitability for use in a photonic devices. At room temperature, the electrical conductivity improved significantly. , accompanied by a decrease in activation energy. Nanocomposites containing 5wt.% Bi_2O_3 demonstrated superior antibacterial activity and additional functions, such as UV protection and free radical scavenging.

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